Anodizing of Aluminum Covered with SiO_2 by Sol-Gel Coating
- Formation mechanism of Composite Oxide Films with High Potential Sustainability -

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Introduction

During galvanostatic anodizing of aluminum in neutral electrolytic solution, a dense barrier type anodic oxide film is formed at a constant growth rate until breakdown occurs. It is of industrial significance in electrolytic capacitor manufacturing to form anodic oxide films, which can sustain voltage higher than 500V. Li et al have reported a breakdown potential over 500V during anodizing in diluted borate solutions, and the growth of anodic oxide films with many imperfections[1]. In a previous study, the authors have investigated the formation of Al-Si composite oxide films by the combination of sol-gel coating and anodizing[2].

In this investigation, the authors examined the effect of borate concentration in anodizing solution on the formation of Al-Si composite oxide films on their dielectric properties.

Experimental

Specimen: Highly pure aluminum (99.99%) foil was used as specimens (2 x 2 cm with handle) and electropolished in perchloric acid / acetic acid mixture.

Sol-gel coating : SiO_2 coating was applied to the specimen by sol-gel dip-coating .The dipping and heating at 573 K were repeated two to 5 times (n=2〜5). Detail of SiO_2 sol preparation and coating process is described elsewhere. [2]

Anodizing: Specimens with / without SiO_2 film were anodized in 0.5M- H_3BO_3 (Solution-I), 0.5M-H_3BO_3 / 0.005M-$Na_2B_4O_7$ (Solution-II), and 0.5M-H_3BO_3 / 0.05M-$Na_2B_4O_7$ (Solution-III) at T_a=333 K with a constant current of i_a=10A m^{-2}. Changes in the anode potential, E_a, with time, t_a were followed with a digital multi-meter connected to PC system. The amount of aluminum ions, W_{Al}, dissolved during anodizing was examined by ICP-AES.

Characterization: SiO_2 films and anodic oxide films were characterized by transmission electron microscopy (TEM), Rutherford backscattering spectroscopy (RBS), electron diffraction (ED), energy dispersive x-ray analysis (EDX), and electrochemical impedance measurement (ECI). In TEM, vertical cross sections of specimens were observed by an ultra thin sectioning technique. In ECI, specimens were immersed in a neutral borate solution at 293K, and 10mV of sinusoidal voltage was applied in the range of 10^{-2}-10^5 Hz.

Results and Discussion

Figure 1 shows the time-variations in anode potential, E_a, and the amount of dissolved Al^{3+} ions, W_{Al}, during anodizing in Solution-II at T_a=333 K for the specimen coated with SiO_2 at n = 4, and for the specimen without SiO_2. Both specimens show a linear increase in E_a with t_a until E_a reaches 550 V, and the slope of the curve for the SiO_2-coated specimen is twice as high as that for the specimen without SiO_2. The dissolution rate for SiO_2-coated specimen is lower than that for the specimen without SiO_2. The current efficiency for film formation can be estimated to be more than 99% for the SiO_2-coated specimen, assuming no gas evolution, and for the specimen without SiO_2 to be 83 %.

Figure 2 shows the TEM images of the vertical cross section of specimens a) coated with SiO_2 at n = 4, and b) anodized to 500 V after SiO_2-coating. An anodic oxide film grows during underneath SiO2-coated layer during anodizing, and the thickness of the SiO_2 layer decreases. EDX and RBS measurements showed that the anodic oxide film consists of two layers: an outer Al-Si composite oxide layer and an inner pureAl_2O_3 layer. The parallel capacitance of the specimen anodized to 500 V after SiO_2 coating was 10 % larger than that without SiO_2 coating.

The decrease in borate concentration in anodizing solution increased the film breakdown potential, and this tendency was more remarkable on SiO_2-coated specimen than on the specimen without SiO_2. The anodic oxide films formed after SiO_2 coating had a relatively small number of imperfections.

Reference

[1] Y. Li, H. Shimada, M. Sakairi, K. Shigyo, H. Takahashi, and M. Seo, *J. Electrochem. Soc.* **144** (1997) 866
[2] K. Watanabe, M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, and S. Hirai, *Submit to J. Electrochem. Soc.*

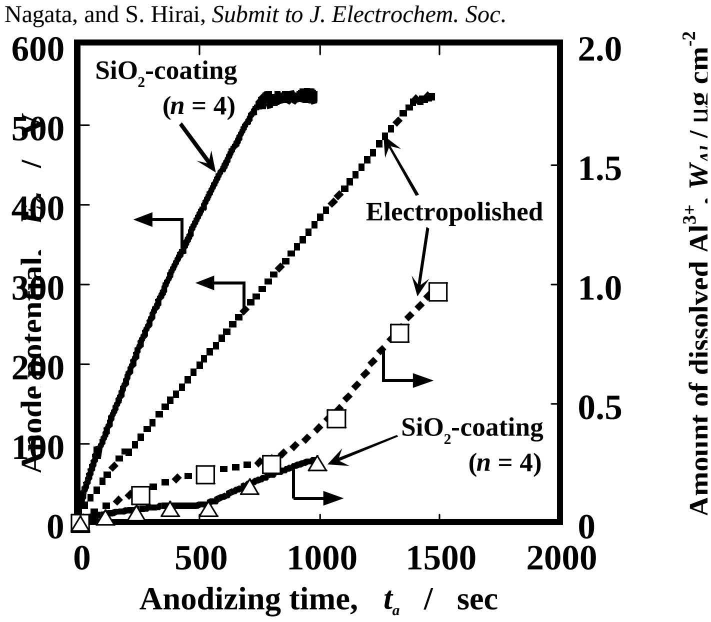

Fig. 1 Changes in anode potential, E_a, and amount of dissolved aluminum ions, W_{Al}, with time, t_a, during anodizing for electroppolished and SiO_2-coated (n = 4) specimens.

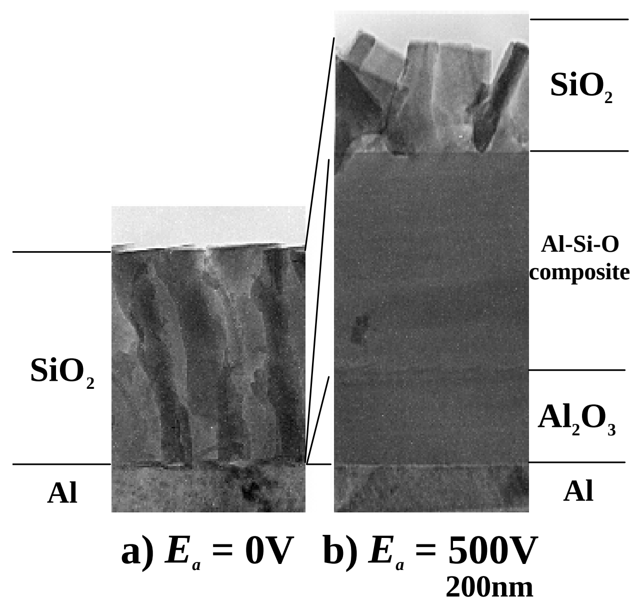

Fig. 2 TEM images of the vertical cross section of specimens a) coated with SiO_2 at n = 4, and b) anodized to 500V after SiO_2 coating